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PROVISIONAL APPLICATION COVER SHEET

To the Commissioner of Patents and Trademarks
Alexandria, VA 22313-1450

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53(b) (2).

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INVENTOR (s) / APPLICANT (s)

Inventor No. 1 of 4	Address:	Citizenship
Last Name: PUSKAS First Name: Judit M.I. E.	1295 Sandy Lane Unit 1215 Sarnia, Ontario Canada N7V 4K5	Canadian
Inventor No. 2 of 4	Address:	Citizenship
Last Name: EBIED First Name: Amer M.I.	148 Clarendon Crescent London, Ontario Canada N6C 5B8	Canadian
Inventor No. 3 of 4	Address:	Citizenship
Last Name: LAMPERD First Name: Barry M.I.	1200 Michener Road Sarnia, Ontario Canada N7T 7H8	Canadian
Inventor No. 4 of 4	Address:	Citizenship
Last Name: KUMER First Name: Bhuwneesh M.I.	455 Platt's Lane Apartment #32 London, Ontario Canada N6G 3H2	Indian

TITLE OF THE INVENTION (280 characters max)

LESS-LETHAL AMMUNITION PROJECTILE

CORRESPONDENCE ADDRESS

Ralph A. Dowell PTO CUSTOMER NO. 000293
DOWELL & DOWELL, P. C.
Suite 309
1215 Jefferson Davis Highway
Arlington, Virginia 22202-3697
Telephone (703) 415-2555
Fax No. (703) 415-2559

STATE	Virginia	ZIP CODE	22202	COUNTRY	United States
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ENCLOSED APPLICATION PARTS (check all that apply)

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Typed or Printed Name: Ralph A. Dowell Registration No.: 26,868

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Legal Representative:

Attorney or Agent: Ralph A. Dowell

Registration Number: 26868

Attorney or Agent: Wendy M. Slade

Registration Number: 53604

Customer Number Correspondence Address: 000293

000293

INVENTOR(s):

Primary Citizenship: Canadian

Given Name: Judit

Middle Name: E.

Family Name: Puskas

Residence City: Sarnia

Residence Country: CA

Address: 1295 Sandy Lane
Unit 1215
Sarnia Ontario, N7V 4K5 CA

Primary Citizenship: Canadian

Given Name: Amer

Family Name: Ebied

Residence City: London

Residence Country: CA

Address: 148 Clarendon Crescent
London Ontario, N6C 5B8 CA

Primary Citizenship: Canadian
Given Name: Barry
Family Name: Lamperd
Residence City: Sarnia
Residence Country: CA
Address: 1200 Michener Road
Sarnia Ontario, N7T 7H8 CA

Primary Citizenship: Indian
Given Name: Bhuwneesh
Family Name: Kumar
Residence City: London
Residence Country: CA
Address: 455 Platt's Lane
Apartment #32
London Ontario, N6G 3H2 CA

UNITED STATES**HILL & SCHUMACHER****Title: LESS-LETHAL AMMUNITION PROJECTILE****Inventors:****Judit E Puskas****Citizenship: Canadian****1295 Sandy Lane, Unit 1215
Samia, Ontario
Canada, N7V 4K5****Amer Ebied****Citizenship: Canadian****148 Clarendon Crescent
London Ontario
Canada, N6C 5B8****Barry Lamperd****Citizenship: Canadian****1200 Michener Road
Samia, Ontario
Canada, N7T 7H8****Bhuwneesh Kumar****Citizenship: Indian****455 Platt's Lane
Apartment # 32,
London, Ontario
Canada, N6G 3H2**

LESS-LETHAL AMMUNITION PROJECTILE

FIELD OF THE INVENTION

The present invention relates to polymeric-based non-lethal ammunition used for the purpose of crowd control and to be used by special task forces, e.g. SWAT teams and/or air marshals. Another aspect of this invention relates to a composite material, which is a thermoplastic elastomer – elastomer blend filled with a higher density constituent.

BACKGROUND OF THE INVENTION

In many types of confrontation situations, the use of lethal ammunition is not appropriate. More and more law enforcement and military authorities are seeking ways to reduce casualties in confrontation situations, particularly crowd control and in hostage situations, which are handled by special task forces, e.g. SWAT teams and air marshals. Different available less-lethal devices have been evaluated and categorized in terms of their effectiveness and potential in the context of law enforcement ("Less Lethal Technologies- Initial Prioritisation and Evaluation," by T. Donnelley, Home Office, PSDB No 12/01, Police Scientific Development Branch, Hertfordshire, United Kingdom (2002)" –with permission to quote). In this report, the impact type of less-lethal ammunition projectiles were placed in Category A, i.e. those devices meriting immediate further research. Examples of less-lethal ammunition projectiles given were bean bags, sock rounds, single and multiple ball rounds, fin stabilized rubber projectiles, single and multiple baton rounds and encapsulated rounds.

Fin stabilized rubber projectiles (referred to as the Rocket) are made of thermoset elastomers, for example EPDM (Ethylene-Propylene-Diene rubber). One specific sample analyzed was made of filled thermoset EPDM and was measured to have a density of 2.44 gcm^{-3} , and Shore A Hardness (ASTM D2240)

of 62. The fin stabilization improves the accuracy at long ranges. These projectiles are generally fired from a 12-gauge shotgun or compressed gas weapon and the typical range is up to 45 m. Drawbacks associated with these types of projectiles are their high fabrication cost and very small tolerances in the design dimensions. In addition, under cold climatic conditions ($< 0^{\circ}\text{C}$) these projectiles 'freeze' i.e., become hard, and as a result can be lethal if for example they hit a person in the head or temple.

Another type of non-lethal ammunition, namely tail stabilized lead filled rubber projectiles (Tube) consist of a cylindrical envelope made of thermoset elastomers, for example EPDM or SBR (styrene-butadiene rubber). The core of the projectile is filled with lead pellets. The tail is attached to the projectile for stabilization, which improves its accuracy. One specific example analyzed was made of filled SBR, and was measured to have a density of about 1.2 gcm^{-3} , and Shore A hardness of 62. These projectiles are generally fired from a 12-gauge weapon and the typical range is 5-30 m, depending on the model and type of weapon used. Drawbacks associated with these types of projectiles are their high fabrication cost, presence of lead and their 'lethality' under cold climatic conditions.

Another type of non-lethal ammunition, mono-ball rounds, consist of single rubber balls which are delivered over a short range. They are made of thermoset elastomers, e.g., natural rubber, filled with mineral fillers, e.g., calcium carbonate. One specific example analyzed was made of filled thermoset polyisoprene (synthetic or natural) and was measured to have a density of 1.11 gcm^{-3} and Shore A Hardness of 46. Drawbacks associated with these projectiles include little or no accuracy. These projectiles are generally fired from a 37 mm weapon, which most police and military personnel find cumbersome to carry around.

Multi-ball rounds are another type of less-lethal impact projectiles which include multiple rubber balls delivered over a short range as these projectiles quickly lose their kinetic energy owing to their low mass. They are made of thermoset elastomers, e.g., natural rubber or SBR, filled with minerals, e.g.,

calcium carbonate or carbon black. One specific example analyzed was made of filled thermoset EPDM, and was measured to have a density of 1.1 gcm^{-3} , and Shore A hardness of 62. These projectiles are generally fired from a 12-gauge weapon but other calibers may also be found. The range of these projectiles depends on the diameter and number of balls, the caliber of the projectiles and the amount of propellant. Drawbacks associated with these projectiles is that like single ball rounds, these projectiles are indiscriminate hence have little or no accuracy.

Beanbag rounds are another type of non-lethal ammunition which consist of a square or circular envelope of fabric containing lead shots. The beanbag is generally fired from a 12-gauge weapon and flattens on impact, thereby spreading the energy over a large area. The typical range is 5-30 m, depending on the model and type weapon used. For example, a 12 gauge round contains two 2-inch beanbags, each filled with 20 grams of #9 Lead. A few shortcomings associated with beanbag projectiles include inaccuracy, failure to open up and hitting the target edge on (i.e., "Frisbee effect"). In addition, the fabric may tear, causing environmentally toxic lead pellets to spill over the target and causing serious injuries. These are the most widely used less-lethal impact projectiles in North America and are associated with few fatal incidents.

Sock rounds, another type of less-lethal impact projectiles were developed to overcome the shortcomings associated with bean bag rounds. The sock round consists of a "sock" filled with lead pellets. A long tail is attached to the sock to enhance the stability of the projectile during flight. The problems associated with sock rounds are inaccuracy, tear of fabric and presence of environmentally toxic lead.

Powder filled rounds are less-lethal impact projectiles made of very soft, highly pliant silicon elastomers filled with metal powder. These projectiles expand radially upon impact thereby spreading their kinetic energy over a large area. The problem associated with these rounds is high cost.

Another type of less lethal ammunition are baton rounds which were first used by the police in Northern Ireland in 1973 and have steadily evolved over the years. They are made of polyurethane-based thermoplastics and have a RHD (ASTM D1415) hardness in the range of 85 to 95 and mass in the range of 90 to 100 g. The most common commercially available rounds are L5A7 and L21A1.

One of the major concerns for law-enforcement agencies in using these less-lethal ammunition projectiles is the delicate balance between their effectiveness and their lethality. For example, the sock rounds, (i.e., fabric filled with lead pellets) and rubber projectiles (i.e., solid or filled with lead pellets) which are presently being used for crowd control, have been found to be lethal within a short range or causing serious injuries to vital organs. The fabric or thermoset elastomer used for the manufacture of these less-lethal projectiles require intricate design and fabrication, which enhances their cost. In addition, the presence of environmentally toxic lead results in serious health safety concerns among law enforcement agencies. Literature survey revealed that less lethal ammunition presently being used are either made of thermoplastics or thermoset based carbon black / calcium carbonate filled composites. They reportedly are capable of inflicting lethal injuries when shot from a short distance or when shot at a vital organ (R. I. H. Whitlock and J. M. Gorman, Int. J. Oral Surg. 7, 240-245 (1978)).

Recently, Cynthia A Bir of Wayne State University, Michigan (Evaluation of Blunt ballistic impacts: The establishment of human response corridors. Bir C A; Vino D C; King A I, Proceedings of the Non-lethal Conference IV, Tysons Corner, VA (2000); Ph. D. Thesis, 2000), has analyzed the effect of blunt ballistic impact on the thoracic region using human cadavers. She determined the human response corridors and developed biomechanical surrogates, which can be used for testing different new projectiles for their blunt ballistic impact. In addition a 3-Rib Ballistic Impact Device (3-RBID) was developed to simulate the human response to low mass, high velocity impacts to the chest region. The human response force corridor for blunt thoracic impact for a 30 g projectile travelling at

60 ms⁻¹ (~ 200ft s⁻¹) was found to be in the range of 1800 N to 3800 N (400 lb_f to 830 lb_f). Based on this work, in the present invention, the optimum weight and impact energy requirements for the new less lethal projectiles were applied for designing the new less lethal projectile. In addition, this invention also presents a new method to measure the impact energy of new and existing less lethal projectile. This new method uses a viscoelastic material, namely polystyrene foam (Styrofoam Impactor) to measure the impact energy of less-lethal projectiles. Traditionally clay or gel are used to measure the impact energy of lethal projectiles. These are also viscoelastic materials, but are very sensitive to environmental conditions such as moisture level and temperature so need to be conditioned before use. The traditional method has been adopted to test less-lethal ammunition as well but due to the low impact force of less lethal projectiles it is not very satisfactory for this purpose.

Related Art

As discussed above, the use of less-lethal projectiles is known. Such less-lethal ammunition are characterized by the use of fillers such as carbon black, calcium carbonate, iron powder, consolidated into a bullet having sufficient density for use in less-lethal ammunition. For example, Patent Application GB 2,192,258 discloses a less-lethal round comprising a projectile made of synthetic polyisoprene. Patent Application FR 2,532,742 discloses projectiles formed of an unspecified rubber bullet having a Shore A hardness of 40 to 55. Projectiles made of filled thermoplastic elastomers TPEs (ethylene-propylene copolymer, styrene-isoprene-styrene SIS or styrene-butadiene-styrene SBS type) have been disclosed (J.C. Gardner, P. G. Gardner, I. P. Oliver and T. Peake, U.S. Patent 5,786,419, Jul. 28, 1998, B. Dubocage and J. Mautcourt (to SNPE Paris Cedex), U.S. Patent 6,295,933 B1, Oct. 2, 2001). All the composites mentioned above are based on either filled thermoset elastomers or filled thermoplastic elastomers; the fillers may include carbon black, calcium carbonate, metal powder or other minerals. The composite material of the present invention is a

blend of an elastomer, a thermoplastic elastomer and a filler, which results in the unique properties of the less-lethal ammunition of this invention.

Design principles of the new projectile

When designing the new projectiles, several considerations should be taken into account. There are optimum material density requirements for any bullet, lethal or less-lethal. In addition, the propellant powders are intended to work with a projectile of a certain mass that provides a typical pressure vs. time curve. Using a lighter projectile causes many problems, the main one being too low energy transfer. Lighter projectiles have to be much faster to provide sufficient energy transfer, which requires a propellant powder that would burn faster. The combination of fast powders and lightweight projectiles can dangerously exceed recognized gun chamber pressure standards. In addition, if higher than desired linear velocity of a projectile is inherently coupled with higher than desired spin velocities, this results in poorer accuracy of the bullet. For projectiles, lower density almost invariably translates into poorer performance in terms of accuracy. With less dense materials, the bullet cannot be brought up to its desired weight by increasing its size due to the dimensional limitations imposed by the standard gun chambers into which the bullet must fit. A bullet that would require re-chambering the gun would not be acceptable to many gun owners because the weapon would no longer be optimal for standard ammunition. Neither of these choices is commercially viable.

Therefore it would be very advantageous to provide a less lethal projective using a material which can be produced using conventional polymer processing technology and which can be reused or recycled.

SUMMARY OF THE INVENTION

The objective of the present invention is to provide a low toxicity, low cost, high-density replacement material for developing novel less-lethal ammunition projectile. This can be achieved by using a compacted mixture of fine iron powder, thermoplastic block copolymer and elastomer. Iron powder having a specific gravity of 7.8 grams per cubic centimeter (gm/cc) cannot be matched with equivalent metals available at an affordable cost. The choice of this composite is the most economic approach to generate a replacement material to solid rubber or lead filled less-lethal ammunition currently available. This replacement material provides added value, such as significantly less toxicity, pollutant and is recyclable.

The present invention provides a composite material made of an elastomer, a thermoplastic elastomer and a filler, which is molded into a less lethal ammunition projectile using conventional polymer processing technology such as compression or injection moulding. The composition disclosed herein provides a highly damping polymer matrix, which is conducive to its use as a less-lethal projectile.

Nano-structured thermoplastic elastomers (TPEs) are emerging materials in the field of polymer science. These materials show processing behavior similar to that of thermoplastics and mechanical properties similar to that of thermoset elastomers or rubbers. Therefore they combine advantages of low fabrication cost and recyclability, i.e., similar to thermoplastics, and low hardness and elasticity i.e., similar to thermoset elastomers. Preliminary testing demonstrates that Polyisobutylene (PIB)- polystyrene (PS) based block copolymer TPEs with their inherent high damping properties would eminently be suitable for developing a composite for novel less lethal projectiles. Moreover, the exceptionally low temperature properties of these block copolymers together with ease of processing and recyclability, makes them suitable candidates. It is an objective of the present invention to provide a low toxicity, low cost, high-density replacement material for presently used less lethal projectile ammunition. This can be best achieved by using a compacted mixture of fine iron powder and of a blend of a

thermoplastic elastomer and an elastomer. This replacement material provides added value, such as significantly less toxicity or pollutant. Since the elastomer phase is not chemically crosslinked, the composite can be recycled, but keeps its shape due to the presence of TPE.

Accordingly, the present invention provides a composite comprising:

(i) a polymer matrix comprising

(a) at least one thermoplastic elastomeric polymer (TPE) component, and

(b) at least one soft elastomeric polymer component; and

(ii) particles of a high specific gravity material are dispersed in the polymer matrix having a density and present in an amount such that the composite has a specific gravity of greater than one, preferably greater than two.

The composites thus prepared are subjected to a molding process, by which cylindrical bodies from the said composite, e.g. projectiles for firearms, etc.

Further features and advantages of the present invention, as well as the structure and operation of various embodiments of the present invention, are described below in detail.

BRIEF DESCRIPTION OF DRAWINGS

The following is a description, by way of example only, of the new projectile, material properties of the composite in comparison with other compositions, and the performance of the novel projectile in comparison with existing less-lethal ammunition, constructed in accordance with the present invention, reference being had to the accompanying drawings, in which:

Figure 1: Design of the new less-lethal projectile with tail for 12 and 20 gauge ammunition.

Table 1: Composition, Shore A hardness and density of various IIR/SIBS/Iron blends

Figure 2: Compression creep of IIR/SIBS/Iron blends.

Figure 3: Storage moduli plots of IIR/SIBS/Iron blends at 50 °C

Figure 4: Tan delta plots of IIR/SIBS/Iron blends at 50 °C.

Figure 5: Storage moduli plots of IIR/SIBS/Iron blends at 0 °C

Figure 6: Tan delta plots of IIR/SIBS/Iron blends at 0 °C

Figure 7: Storage moduli plots of IIR/SIBS/Iron blends at -50 °C

Figure 8: Tan delta plots of IIR/SIBS/Iron blends at -50 °C

Figure 9: Comparison of the storage moduli plots of existing less-lethal ammunition projectiles and SIBS50 at 50 °C.

Figure 10: Comparison of the tan delta plots of existing less-lethal ammunition projectiles and SIBS50 at 50 °C.

Figure 11: Comparison of the storage moduli plots of existing less-lethal ammunition projectiles and SIBS50 at 50 °C.

Figure 12: Comparison of the tan delta plots of existing less-lethal ammunition projectiles and SIBS50 at 50 °C.

Table 2.-Accuracy and impact energy for the new 20-gauge less-lethal projectiles

Table 3. Accuracy and impact energy for 20-gauge sock-round less-lethal projectiles

Table 4. Accuracy and impact energy for the new 12-gauge less-lethal projectiles.

Table 5. Accuracy and impact energy for 12-gauge sock-round less-lethal projectiles

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

Definitions

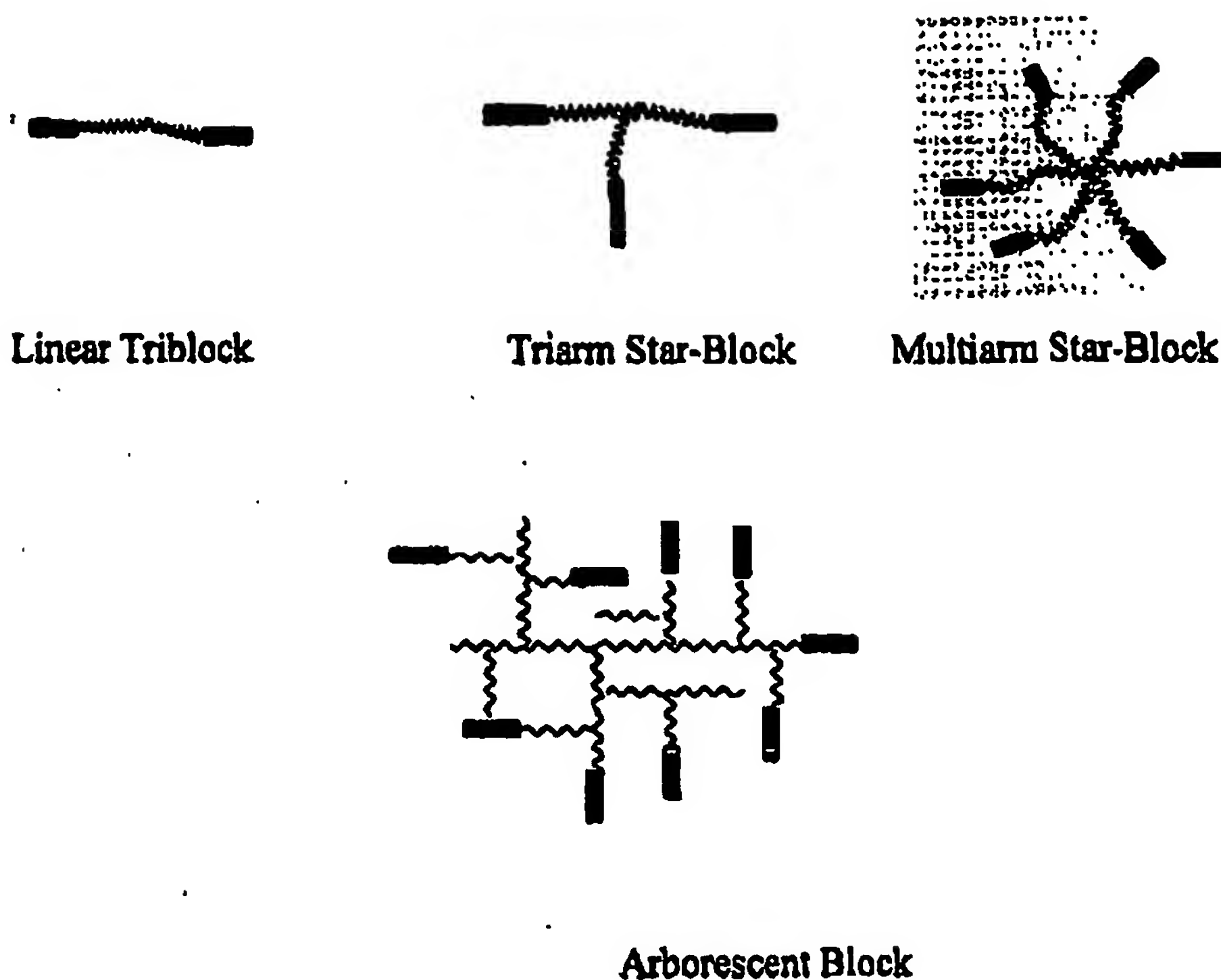
As used herein, the term "soft elastomeric" means a polymer that at ambient temperatures is above its glass transition temperature (first order transition temperature). In other words, this material is one which at ambient temperatures is a viscous material having an amorphous structure. It is this component of the polymer matrix which is primarily responsible for the softness and high damping characteristics of the final composite.

As used herein, the term "elastomeric thermoplastic polymer" means a thermoplastic polymer that at ambient temperatures exhibits a suitable degree of resilience and/or hardness such that those properties of the final polymer matrix are increased compared with those physical properties of the soft elastomeric polymer component alone. It is the thermoplastic nature of this second thermoplastic polymer component of the matrix of the composite which is primarily responsible for the hardness and/or low compression creep properties of the final composite.

Figure 1 shows the dimensions of the 12 and 20-gauge projectiles. In terms of impact, the most important design criterion is the maximum tolerable energy or force per unit area that an average human could withstand without serious injury. This is highly individual as it generally depends on the individual's body fat and muscle mass. Bir's study considered the average male (about 5 ft 10 in, 160 lb). Based on her results, the tolerable energy transfer at muzzle is 44 J 32 (ftlb) for the 20 gauge and 73 J (54 ftlb) for the 12-gauge projectile. The maximum allowable deflection of 6.93 mm and the maximum tolerable energy transfer on impact without serious injury is limited to 3200 N. With the desirable 76 ms⁻¹ (250 ft/s) muzzle velocity, this translates into about 15 g and 25 g weight for the 20 and 12-gauge projectiles, respectively. Thus the minimum density of the projectiles with the dimensions shown in Figure (1) was calculated to be 2.4 gcm⁻³.

The next criterion was the selection of materials that would yield the desired mechanical properties. Butyl elastomer (IIR) has outstanding low temperature properties and very high damping, but has very high creep without crosslinking (J. V. Fusco and P. House, in "Rubber Technology," M. Morton, Ed., Van Nostrand Reinhold Company, New York (1987)). It was theorized that a blend of novel polyisobutylene-based styrene-isobutylene-styrene SIBS TPE (J. P. Kennedy, J. E. Puskas, G. Kaszas, and W. G. Hager (to the University of Akron) U.S. Patent 4,946,899, Aug. 7, 1990), and butyl elastomer, filled to achieve the required minimum density of 2.4 cm^{-3} , would be a promising composite for less-lethal ammunition. TPEs, including SIBS, show processing behavior similar to that of thermoplastics and mechanical properties similar to that of thermoset elastomers or rubbers. Therefore they combine the advantages of low fabrication cost and recyclability with elasticity and softness (G. Holden and N. R. Legge, in "Thermoplastic Elastomers-A Comprehensive Review," G. Holden, N. R. Legge, R. Quirk, H. E. Schroeder (Eds.), Hanser Publishers, Munich (1996)).

Styrenic block-type thermoplastics elastomers (SBS and SIS) have been commercialized since the 1960s and are available in a wide range of hardness, depending on the rubber/plastic ratio. SIBS have been developed in the last decade and only recently have been commercialized. Preliminary testing demonstrated that SIBS with its inherent high damping properties due to the polyisobutylene segment would eminently be suitable for developing a composite for the novel less-lethal projectiles. Moreover, the exceptional low temperature properties of these block copolymers together with ease of processing and recyclability, make them suitable candidates for low temperature application. The SIBS would provide a "physically crosslinked network", thereby ensuring shape retention combined with recyclability. With the advent of macromolecular engineering, scientists gained control over polymerization processes and are able to produce various polymer architectures, shown in Scheme 1:



Linear triblock SIBS TPEs are considered the first generation of these new materials and were introduced commercially in 2003 by Kaneka Co. of Japan, based on a license of U.S. Patent 4,946,899, from the University of Akron. Star-branched SIBS is considered the second generation, with improved properties, and has not been commercialized yet. The third generation, arborescent (dendritic, tree-like) SIBS TPEs in 2002 (J. E. Puskas, P. Antony, C. Paulo U.S. Patent application). Initial investigations of the mechanical and viscoelastic properties of these materials indicated superior properties (P. Antony, Y. Kwon, J. E. Puskas, M. Kovar, P. R. Norton, EUR. POLYM. J., in press (2003)). All of these SIBS-type TPEs can serve as "physical crosslinking agents" of the butyl (IIR) elastomer matrix of the current invention. Any type of commercial butyl elastomer can be used as the elastomeric component of the composite in the present invention.

In order to achieve the desired density of the composite, an appropriate filler needed to be found. As stated earlier, the use of lead in the less-lethal

market was not favourable, due to its environmental toxicity. Choices of metal powders included tungsten, copper, bismuth, iron and iron oxides. The Brinell Hardness for tungsten and copper was 2670 MNm^{-2} and 874 MNm^{-2} , respectively, hence these were considered too abrasive and would damage the barrel of the gun. Though the Brinell Hardness of bismuth was 94.2 MNm^{-2} , it was too expensive in comparison with iron. Iron oxide had a density of 5.24 g/cm^3 , which was not high enough for this application. The final choice was iron powder with Brinell Hardness of 490 MNm^{-2} and a density of 7.86 gcm^{-3} .

The present invention, and preferred embodiments of the various aspects thereof, will now be described in detail. The essence of the present invention lies in a special bi-component polymer matrix that provides the composite with desirable balance of physical properties, notably hardness and compression creep and high-damping property combination with required high density. The polymer matrix of the composite of this invention comprises at least one soft elastomeric polymer component and at least one elastomeric thermoplastic polymer component.

Suitable polymers for use in the invention as the soft elastomeric polymer component include polyisobutylene, polyisobutylene-isoprene copolymers, polyisobutylene-styrene copolymers, polyisobutylene-alkyl styrene copolymers, halogenated polyisobutylene-alkyl styrene terpolymers, polybutadiene, polyisoprene, polyethylene-propylene copolymers, polyethylene-propylene diene terpolymers. Polyisobutylene, polyisobutylene-isoprene copolymers, particularly preferred. Selection of an optimum polymer may depend upon the exact mechanical properties required of it, which may depend to at least some extent on the amount of it to be incorporated in the polymer matrix and the relative physical properties of the elastomeric polymer component, and possibly any other components of the composite which are present, including the high specific gravity weight material dispersed therein.

Preferred elastomeric thermoplastic polymers for use in the polymer matrix are block copolymers comprising at least one amorphous elastomeric unit species. Examples of block copolymers of this type include polystyrene-polybutylene block copolymer, polystyrene-polyethylene block copolymer, polystyrene-polybutadiene block copolymer and polystyrene-polyisoprene block copolymer.

Preferably, the rigid thermoplastic polymer component should be fusible, in order that they may be readily blended with the other polymer component or components of the composite and with the high specific gravity weight material to be dispersed within the matrix of bi-component polymer matrix. Preferably, the rigid thermoplastic polymer component of the matrix has a melting transition temperature (second order transition) of less than about 150°C. This temperature represents the preferred maximum melting point of the rigid thermoplastic polymer component of the matrix.

Polymers of this type are commercially available, for example as the KRATON (trade mark) series of polymers from Shell Chemical Company (for example the KRATON D and KRATON G ranges of polymers) and the Kaneka (trade mark) series of polymers (e.g. Kaneka SIBS 73T and Kaneka SIBS 103T) from Kaneka Corporation, Osaka, Japan.

The high specific gravity weight material is present in the composite of the invention in particulate form and may be added to the polymer matrix during manufacture in the form of a powder or grains thereof. Small particles are preferred, for example having sizes in the range from about 71.4% of -100 to +325 U.S. Mesh and 23.2% of -325 U.S. Mesh, specific gravity, 7.8 gcm⁻³. Within the above preferred criteria, therefore, any particulate high specific gravity material may be used as this component of the composite of the invention. One particularly preferred example of such a material which has been found to be useful in the invention is iron powder, which is non-toxic and itself has a very high specific gravity.

Generally speaking the particulate high density weight material will be present in an amount only sufficient for raising the density of the composite to the

required value, and no more than this. A density of the final composite of at least about 2 or 3 gcm⁻³, where 2.4 gcm⁻³ is preferred density. The amount of powdered iron (or other high density weight material) to be added to the basic polymer blend matrix to achieve this value is a simple matter of calculation or trial and error. Typically, however, the high density weight material may be present in the final composite in an amount of from about 50 to about 90% by volume of the total composite, preferably from about 60 to about 80% by volume, more preferably from about 60 to about 70% by volume, the balance being the polymer matrix.

The composite of the polymer blend matrix, however, is more critical in terms of the balance of physical properties of the individual components, as in order to achieve optimum hardness, strength, compression creep, it is generally important that the content of the softer, elastomeric component is not too high or too low compared with the content of the harder thermoplastic elastomer polymer component.

The polymer matrix of the composite of the invention preferably comprises the soft elastomeric polymer component in an amount within the range from about 25 to about 100 by volume of the polymer matrix, more preferably from about 50 to about 75% by volume, and the elastomeric thermoplastic polymer component in an amount within the range from about 25 to about 50% by volume, more preferably from about 45 to about 55% by volume.

Preferably the high density composite of the invention has a hardness value, as measured according to the Shore D scale, in the range of from about 15 to about 55. A hardness of less than about 30 Shore D gives a product which is generally too soft for applications such as shot or bullets for firearms, where the projectile would tend have compression creep higher than 20% which makes them unsuitable as they have higher probability of getting stuck in the barrel.

The composite of the present invention may be manufactured by conventional methods well known in polymer technology, as are well known to the person skilled in the art and well described in the literature. For example, the rigid thermoplastic elastomeric polymer and soft elastomeric polymer

components are heated to above their melting temperature and one of these components added to the other with mixing in a standard type of mixer until a completely homogeneous matrix is formed, optionally with further heating if necessary. Once the matrix is fully mixed and while the mixture is still in its molten or at least soft state, the particulate high specific gravity weight material is added, with further stirring or mixing in order to evenly disperse the particles in the matrix. Stirring or other form of mixing may be continued until complete dispersion is achieved, following which the composite may be cooled and passed to the next processing stage, which is preferably the formation of discrete bodies of the composite by molding.

The invention present invention will be further illustrated by the following Examples, which are not to be construed as limiting the scope of the present invention in any way.

Example 1

Butyl elastomer (IIR, grade RB301, unsaturation = 1.6 mole %, Mooney viscosity $ML_{1+8} = 125$ °C = 51) which is a commercial elastomer, known in the art and iron-oxide powder (Fe_2O_3 , 20 mesh from Ironics) in 30:70 weight ratio were mixed in a laboratory internal mixer (Haake Rheocord model "Rheomix 3000") with cam type rotors operating at 35 rpm at an initial temperature of 160 °C. The temperature was maintained at 160 ± 10 °C by using a air-cooling system. The density of the composite was 1.51 g/cm^3 , less than the desired density of 2.40 gcm^{-3} . At this density, the weight of the projectile will be less than required hence not suitable for use in less lethal ammunition.

Example 2

Iron powder (Atomet 67, Quebec Metal Powders) and butyl elastomer (grade RB301) in 70: 30 weight ratio were mixed into a composite in a laboratory internal mixer (Haak Rheocord model "Rheomix 3000") with cam type rotors

operating at 35 rpm at an initial temperature of 160°C . The temperature was maintained at $160 \pm 10^{\circ}\text{C}$ by using an air-cooling system. The Shore A hardness of this composite, hereafter referred to as IIR (see Table 1), determined according to ASTM standard D2240, was 18.6 and its density was 2.40 g/cm^3 , sufficient for the less lethal ammunition projectiles shown in Figure 1 which shows the design of the new projectile with tail for 12 and 20 gauge ammunition.

The compression creep of IIR determined by DEFO with 75 Newton load and at 40°C , was 32% (Figure 2).

Compression creep data provides information on the ability of the material to maintain its shape. High creep means high permanent deformation. A thermoset (crosslinked) rubber typically has about 5 % creep, corresponding to excellent ability to maintain the shape of the article. A typical thermoplastic elastomer has somewhat higher creep (10-15%), still associated with good shape retention. Materials with creep higher than 20% would have poor shape retention. (J. V. Fusco and P. House, in "Rubber Technology," M. Morton, Ed., Van Nostrand Reinhold Company, New York (1987).)

Example 3

Example 2 is repeated, with the following modifications. Iron powder (Atomel 67), butyl elastomer (grade RB301) and polyisobutylene-polystyrene block co-polymer (Kaneka grade SIBS073T) in weight ratios (iron:elastomer : block co-polymer, 70 : 22.5 : 7.5) were mixed into a composite material. The Shore A hardness of this composite, hereafter referred as SIBS25, determined according to ASTM standard D2240, was 23 and the density was 2.42 gcm^{-3} . The compression creep of SIBS25 determined by DEFO, at a load of 75 Newton and 40°C was 22% (Figure 2).

Example 4

Example 2 is repeated, with the following modifications. Iron powder (Atomet 67), butyl elastomer (grade RB301) and polyisobutylene-polystyrene block co-polymer (Kaneka grade SIBS073T) in weight ratios (iron:elastomer : block co-polymer, 70 : 15 : 15) were mixed into a composite material. The Shore A hardness of the composite, hereafter referred as SIBS50, determined according to ASTM standard D2240, was 36 and its density was 2.44 g/cm². The dynamic mechanical compression creep of SIBS50 determined by DEFO, at a load of 75 Newton and 40°C was 12% (Figure 2).

Example 5

Example 2 is repeated, with the following modifications. Iron powder (Atomet 67), butyl elastomer (grade RB301) and polyisobutylene-polystyrene block co-polymer (Kaneka grade SIBS073T) in weight ratios (iron: elastomer: block co-polymer, 70: 7.5: 22.5) were mixed into a composite material. The Shore A hardness of the composite, hereafter referred as SIBS75, determined according to ASTM standard D2240, was 44.0 and the density was 2.46 g/cm². The dynamic mechanical compression creep of SIBS75 determined by DEFO, at a load of 75 Newton and 40°C was 11% (Figure 2).

Example 6

Example 2 is repeated, with following modifications. Iron powder (Atomet 67) and polyisobutylene-polystyrene block co-polymer (Kaneka grade SIBS073T) in weight ratios (iron: block co-polymer, 70: 30) were mixed into a composite material. The Shore A hardness of the composite, hereafter referred as SIBS100, determined according to ASTM standard D2240, was 53.3 and the density was 2.49 g/cm². The dynamic mechanical compression creep of SIBS100 determined by DEFO, at a load of 75 Newton and 40°C was 4% (Figure 6).

Exempl 7

Dynamic Mechanical Analysis studies were conducted for IIR, SIBS50, SIBS75 and SIBS100. SIBS25 was not included, since it showed excessive creep (see Example 2). using an MTS Instrument, at 1% strain in a frequency range of 0.15 to 500 Hz at 50 °C. The MTS 831 Elastomer Test System, by MTS Systems Corporation U.S.A., was employed for high frequency dynamic characterization of the composites in the frequency range of 0.01 to 500 Hz. The analysis was carried out on compression molded cylindrical specimens (diameter, 10 mm and height, 10 mm). The DMTA analysis examines the temperature and frequency dependent behavior of materials. In DMTA analysis, application of a stress imposes a deformation or in other words a small strain and the resultant stress developed on the material is measured, which in turn provides the stiffness and damping property of the material. This analysis produces sample environments to characterize material that mimics their end use conditions. The analysis is used for design criteria, quality assurance, comparative investigations and product development / optimization. Figures 3 and 4 show the results of dynamic mechanical analysis. The storage modulus of the material refers to its elastic behavior, which would have significance in its impact properties. The storage modulus (E') gradually increased with frequency for all composites (Figure 3). The plots of SIBS50 and SIBS75 run close and somewhat above the plot of IIR, but both of them are considerably lower than the SIBS composite in the whole frequency range, with the difference increasing at higher frequencies. At higher frequencies, there is no considerable flow of polymer chains within the short period of oscillation and the material behaves like a glassy solid, hence an increase in E' with frequency is observed. All the elastomeric composites showed more or less same tan delta (Figure 4) at higher frequencies, but the IIR composite showed higher tan δ at lower frequencies. The tan delta increase of the composites at high frequency could be due to partial breakdown in the physical cross-links. In the previous Example 3 it has

been shown that incorporation of SIBS polymer to the composite is essential for the shape retention of the less lethal ammunition. In addition to this incorporation of SIBS thermoplastic elastomer also increases the modulus of the composite. If the bullet made from polymer-metal has modulus higher than the desired value, it would be hard and would impart higher energy to the target and can become lethal. Whereas, if the modulus of the composite is less than desired, the less lethal projectile made out of it would become ineffective. With addition of SIBS thermoplastic elastomer the shape retention property and the modulus of the polymer-metal composite can be simultaneously optimized as per requirement and the polymer-metal composite can be used for making a less lethal ammunition.

Example 8

Dynamic Mechanical Analysis was carried out at 0 °C (Figures 5 and 6). E' slightly increased below 1 Hz, followed by a rapid increase and leveling off at about 100 Hz (Figure 5). At 0 °C and higher frequencies, there is no flow of polymer chains within the short period of oscillation hence the modulus increases with frequency. All the elastomeric composites had more or less same tan delta (Figure 6), which gradually increased in the higher frequency range (1 - 500 Hz). This again could be due to the partial breakdown in the physical cross-links.

Example 9

Dynamic Mechanical Analysis was carried out at -50 °C (Figures 7 and 8). The storage modulus plot of the SIBS50 composite was practically identical to the plot of IIR, with SIBS75 and SIBS100 showing higher moduli in the entire range (Figure 7). The tan delta plots of all composites are about the same (Figure 8), decreasing up till about 10 Hz and leveling off in the higher frequency range.

In summary, these results show that IIR and SIBS25 have low Shore A Hardness (Table I), but display high compression creep behavior. SIBS75 had almost the same compression creep as SIBS50 composite but had higher Shore A Hardness and moduli. SIBS100 had lower compression creep and higher Shore A Hardness than the other composite mixes. Based on this analysis the SIBS50 (IIR/SIB/Iron 50/50/233) seems to have optimum hardness, compression creep and dynamic mechanical properties for less-lethal ammunition projectile application.

Example 10

Comparative dynamic mechanical analysis between different existing less lethal ammunition and the newly developed less lethal ammunition was carried out with the MTS instrument, at a dynamic load of 1% strain in a frequency range of 0.15 to 500 Hz at 50 °C and 0 °C (Figures 9-12). At 50 °C, SIBS50 showed lower modulus compared to rocket, tube and mono-ball projectiles (Figure 9). The tan δ of SIBS50 was lower than that of the rocket projectile and the tube projectile but slightly higher than the mono-ball projectile up to about a 100 Hz, beyond which both of the mono-ball and SIBS50 showed increasing but similar tan δ values (Figure 10). At 0 °C, the E' plot of SIBS50 runs below the plots of the rocket projectile and the tube projectile, and close to that of the mono-ball projectile until about 10 Hz (Figure 11). In the higher frequency range (10- 500 Hz), the modulus of SIBS50 showed a sharp increase, reaching the values of the rocket projectile. The tan δ (Figure 12) of the new less-lethal ammunition projectile was somewhat lower than the rocket and tube projectiles, but higher than the mono-ball, up to about 10 Hz, when it started to increase, surpassing the existing projectiles. This indicates very good low temperature properties in the high frequency range.

At -50 °C, it was not possible to measure the dynamic mechanical analysis for rocket and tube projectiles since their modulus exceeded the force limit of the load cell of the instrument.

The dynamic mechanical analysis in the temperature range of 50 – 0 °C, indicates that at higher frequencies the new projectile has lower modulus, indicating lower hardness and higher tan delta, with better damping properties than the existing rocket and tube projectiles.

Example 11

New method for comparative impact testing

The composite SIBS offers the most advantages in terms of compression creep properties (11% DEFO) and hardness (36 Shore A). A comparative impact testing of the new less lethal ammunition projectile developed using SIBS50 (described in Example 4) was carried out using a novel DOW Styrofoam Impactor. The Impactor arrangement consists of polystyrene foam sheets (commercially named Styrofoam SM made by DOW). It is a viscoelastic material allowing for penetration of rubber projectiles. Four 2'x 2'x 2"-sheets are placed upright and strapped tightly to insure a proper hold. The stack of sheets is then placed against a fixed surface such as a brick wall to prevent tumbling. Current tests show that at 15-feet firing distance from the muzzle and 300 ± 15 ft/sec muzzle velocity (measured using a Doppler Radar) results in a penetration of about 6 inches in the foam. Impact Energy transfer is then calculated as a function of the projectile's penetration in the foam by the following equation:

$$\text{Impact Energy (J)} = A \times L_p \times \text{Compressive Strength (0.21 MPa)}$$

Where:

- A = projectile's impact cross sectional area.

L_p = length of projectile penetration in the foam.

The accuracy and the impact energy of less-lethal projectile made of SIBS50 were compared with sock rounds for 12-gauge and 20-gauge projectiles; Tables 2-5 summarize the results. The sock round was selected for this comparative test since it is the most widely used less lethal projectile in market and has proven to be the best of all existing less lethal projectiles, despite of being associated with some serious injuries to human targets ref?. The calculated impact energies were compared with the impact energy corridors proposed by Bir. The clay impactor set-up used by Bir requires significant conditioning at a very narrow temperature and humidity range, thus its use is rather cumbersome. We tested the projectiles using the novel Styrofoam impactor introduced here. Styrofoam is an insulating hydrophobic viscoelastic material that maintains constant mechanical properties over a broader range of temperatures and humidity.

Tables 2 and 3 summarize test results for the 20-gauge less-lethal projectiles. The projectile distance from center of target was 9.30 ± 2.00 cm with an average velocity of 84 ± 5.27 ms⁻¹ for the new projectile, and 7.24 ± 3.28 cm with an average velocity of 91.91 ± 7.17 ms⁻¹ for the sock round. One of the main factors in judging the performance of less-lethal projectiles is its velocity consistency. A velocity deviation less than 10% is regarded excellent when using less-lethal projectiles. The velocity deviation for the newly developed 20-gauge projectile was about 6.3%, in comparison with about 7.8% for the sock round. The second main factor is the impact area of the projectile. Both the newly developed 20-gauge projectiles and the sock rounds impacted in the 10.16 cm (4 in) diameter circle from about 5 m (15 feet), but the sock rounds showed much higher standard deviation. In addition, it was observed during this test that some of the sock rounds failed to open up upon launching and ended up hitting the foam impactor while still folded. Under optimum conditions, a sock round must open within 2 m of launching in order to allow for a higher air resistance and therefore slow down in order to transfer less energy before hitting the target. In the case of the 12-gauge projectiles, tests were carried out from a common police and military firing distance of 10.7 m (~35 ft) using a standard 12-gauge

shotgun. Tables 4 and 5 summarize test results. The velocity deviation computed to about 4% and 7% and the projectiles impacted in the 10.16 cm (4 in) diameter circle. These results are excellent in terms of velocity consistency, but the accuracy became poorer for both the new projectiles and the sock rounds. The new Styrofoam Impactor employed for measuring the impact energy of the less-lethal projectiles yielded favorable results in comparison to the comprehensive study conducted by Bir who employed the Abbreviated Injury Score (AIS), a scale developed in the 1960s to standardize the severity of injuries such as blunt thoracic impact. An AIS value of 0 is equivalent to a minor injury and 6 is equivalent to untreatable injury. It was noted, however, that injuries with an AIS of 3 or larger result in a high probability of death. For example, an injury of lung contusion with hemomediastinum is considered an AIS 4 injury. Using this scale to evaluate the injuries of the 37 mm ammunitions she tested on human cadaver specimens resulted in the development of tolerable force-time corridors and tolerable deflection-time corridors. The tolerable force corridor for a 37 mm projectile weighing 30 g and traveling at 60 ms^{-1} with an impact time of 0.275 ms was between 1800 to 3700 N, which can be translated into an impact energy range of 2.57 to 25.64 J. Under these conditions the average muzzle energy was observed to be approximately 54 J. These data corresponds to an AIS injury of less than 3.

As shown in Table 2 the average impact energy for the newly developed 20-gauge less-lethal projectile was $8.84 \pm 1.70 \text{ J}$ at a muzzle energy of about $47.71 \pm 5.97 \text{ J}$. This impact energy value is closer to the lower boundary set by Bir's actual cadaver testing. For the sock rounds, the average impact energy was $21.88 \pm 1.65 \text{ J}$ at a muzzle energy of about $140.96 \pm 25.15 \text{ J}$ (Table 3). This impact energy is closer to the upper boundary set by Bir's actual cadaver testing. This implies that sock rounds may cause serious injuries if projectiles are fired from shorter distances.

The 12-gauge rounds were fired from a shotgun with more muzzle energy to compensate for the longer distances they travel before impacting the target.

They also weigh more than the 20-gauge rounds. The 23 g 12-gauge new less-lethal projectile leave the muzzle with 89.12 ± 7.19 J energy to impact with 12.32 ± 3.08 J energy from approximately a 10 m distance (Table 4). The impact energy here is still near the lower boundary limits published by Bir.

The 12-gauge sock round with 119.07 ± 16.14 J of muzzle energy had an impact energy of 22.75 ± 1.94 J (Table 5). This was slightly higher than the upper boundary limit, i.e., 25.64 J, set by Bir. With this type of energy transfer, there is greater probability of causing serious injuries to human targets.

In summary, the newly developed less lethal projectiles performed well in comparison with the most frequently used sock rounds in terms of accuracy and velocity consistency, while delivering impact energies close to the lower boundary of the tolerable energy corridors developed by Bir. The impact energy delivered by the sock rounds was closer to the upper limit, with the 12-gauge round surpassing the limit.

Example 12

A comparative accuracy testing of the new less lethal ammunition projectile developed using SIBS50 (described in Example 4) with existing less lethal ammunitions was carried out. In this test, accuracy of several existing ammunition was measured using various weapon systems. For the Rocket and triple ball projectile, a 12-gauge shotgun was used, for the Mono Ball projectile a 37 mm launcher was employed and a 20-gauge handgun was used for the new projectiles. Firing of all projectiles was conducted at a distance of approximately 15 Feet. Table 6 summarizes the results.

Table 6: Accuracy tests for existing and new lethal ammunition projectiles.

Projectile Type	Average distance from target (cm)	Standard Deviation
Rocket	3.2	1.41
Triple Ball	6.3	2.66
Mono Ball	9	3.08
New	3	0.8

The new less lethal projectiles showed better accuracy than the existing less-lethal ammunitions.

As used herein, the terms "comprises", "comprising", "including" and "includes" are to be construed as being inclusive and open ended, and not exclusive. Specifically, when used in this specification including claims, the terms "comprises", "comprising", "including" and "includes" and variations thereof mean the specified features, steps or components are included. These terms are not to be interpreted to exclude the presence of other features, steps or components.

The foregoing description of the preferred embodiments of the invention has been presented to illustrate the principles of the invention and not to limit the invention to the particular embodiment illustrated. It is intended that the scope of the invention be defined by all of the embodiments encompassed within the following claims and their equivalents.

THEREFORE WHAT IS CLAIMED IS:

1. A composite comprising:

a polymer matrix including at least one thermoplastic elastomeric polymer (TPE) component, and at least one soft elastomeric polymer component; and particles of a high specific gravity material are dispersed in the polymer matrix having a density and present in an amount such that the composite has a specific gravity of greater than one.

2. The composite material according to claim 1 subjected to a molding process, by which cylindrical bodies are produced from the said composite.

ABSTRACT

A high-density composite material and its use in the manufacture of less-lethal ammunition projectile is disclosed. The composite ammunition projectile material consists of a compact mixture of fine iron powder, a highly damping, inert, non-toxic elastomer and an inert non-toxic thermoplastic elastomer. The composite ammunition projectile material is first blended, then the bullet is injection molded or compression molded. The density of the composite ammunition projectile material is adjustable in terms of ratio of iron powder to elastomer to thermoplastic elastomer block co-polymer.

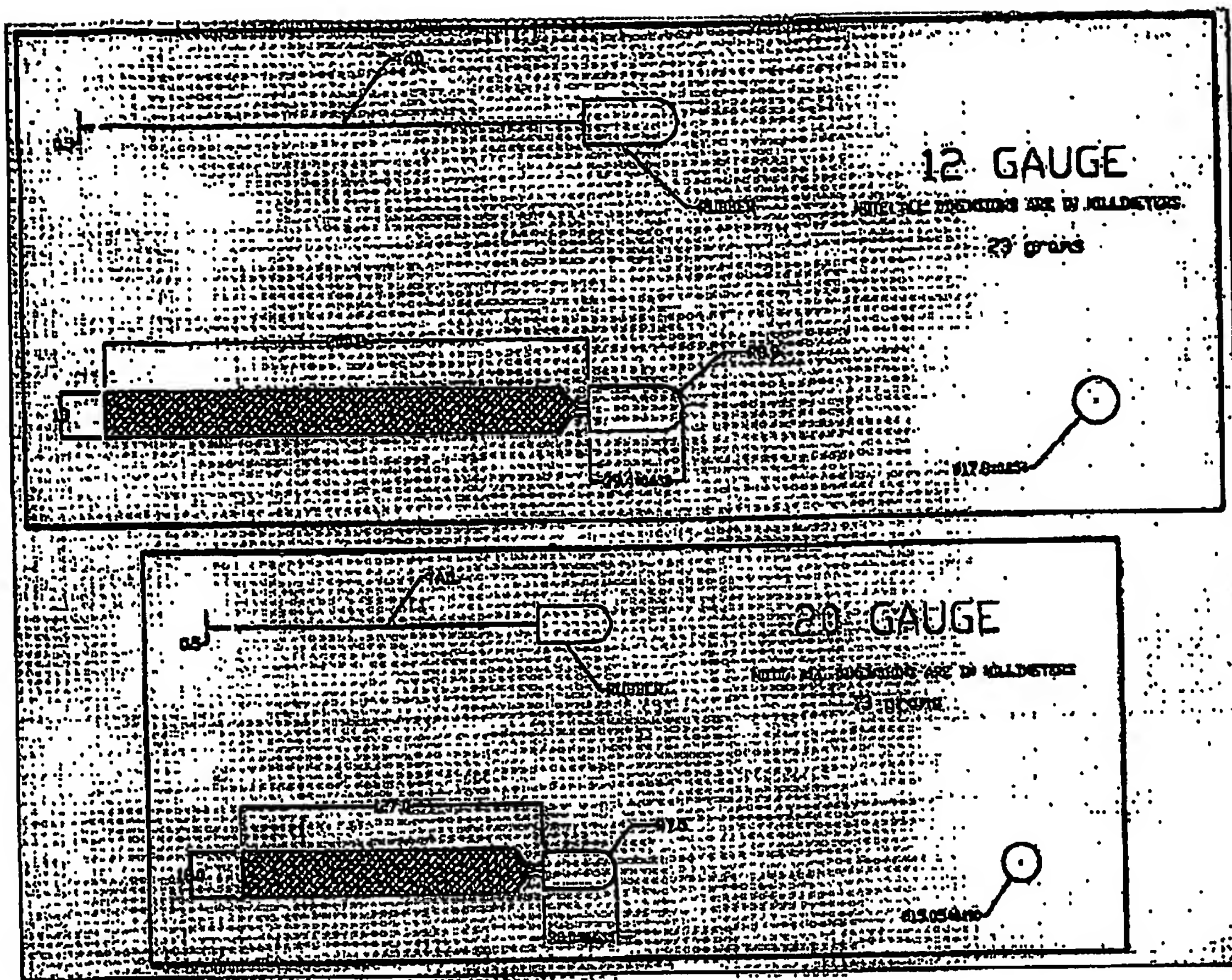


FIGURE 1

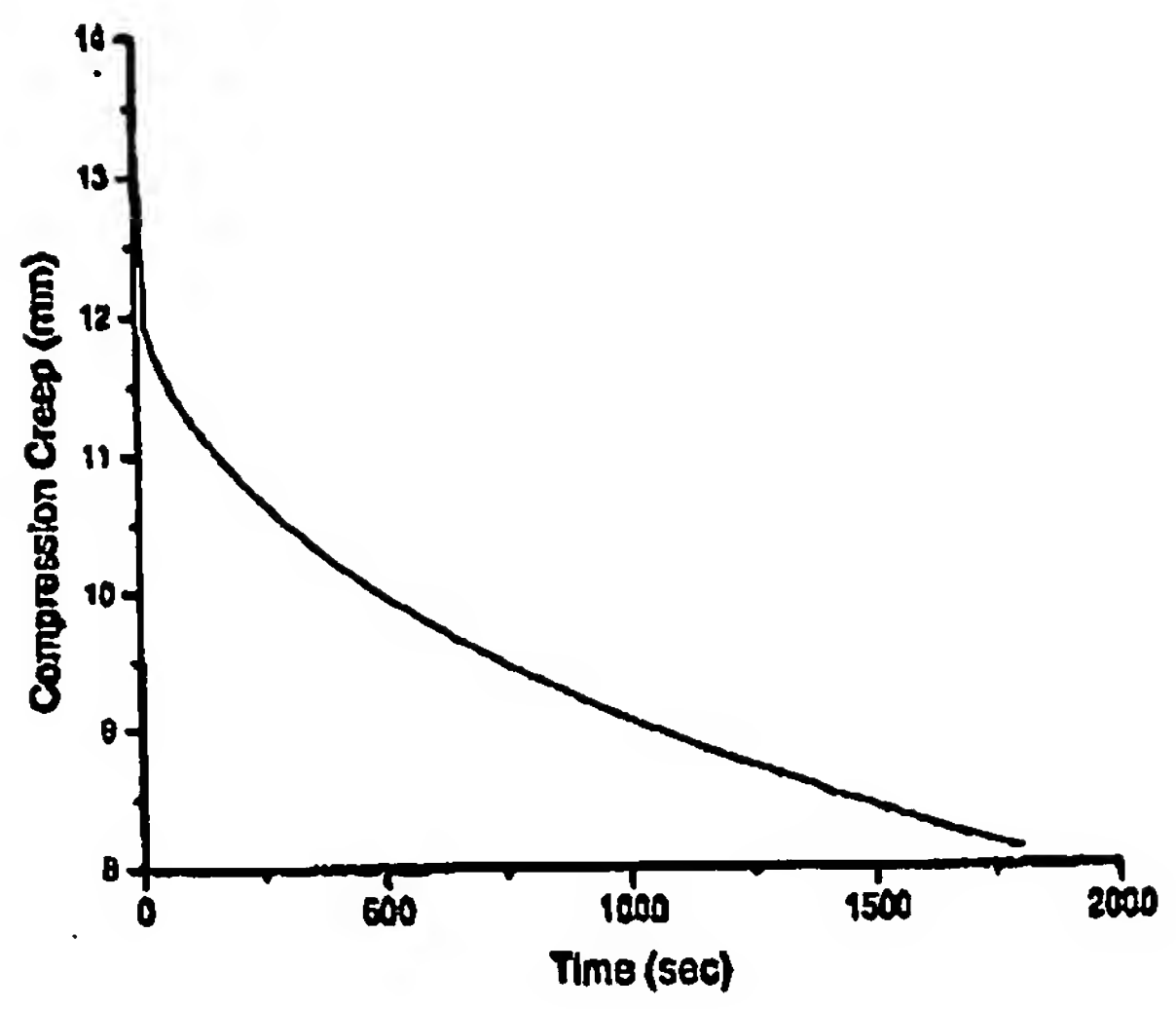


FIGURE 2

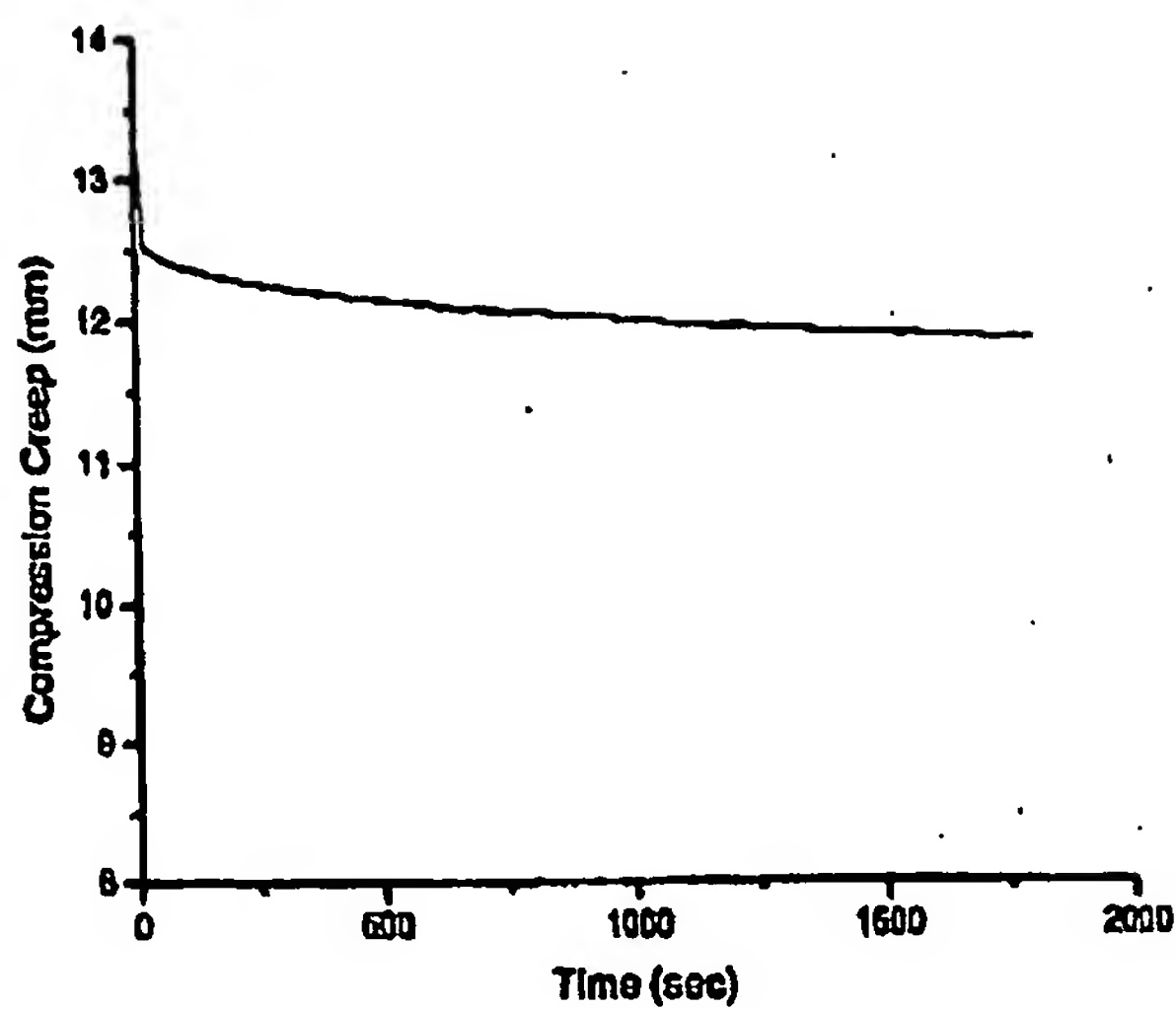


FIGURE 4

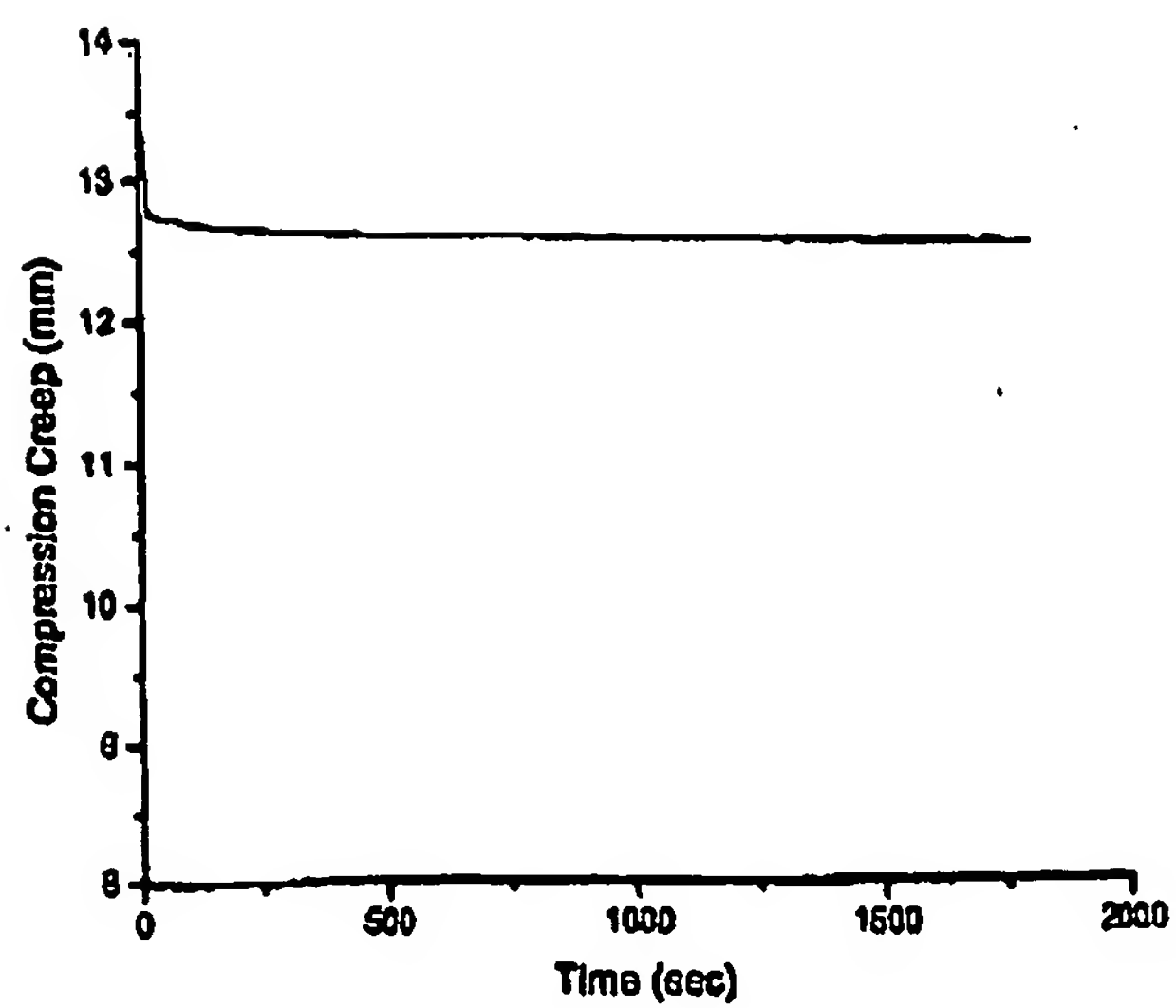


FIGURE 5

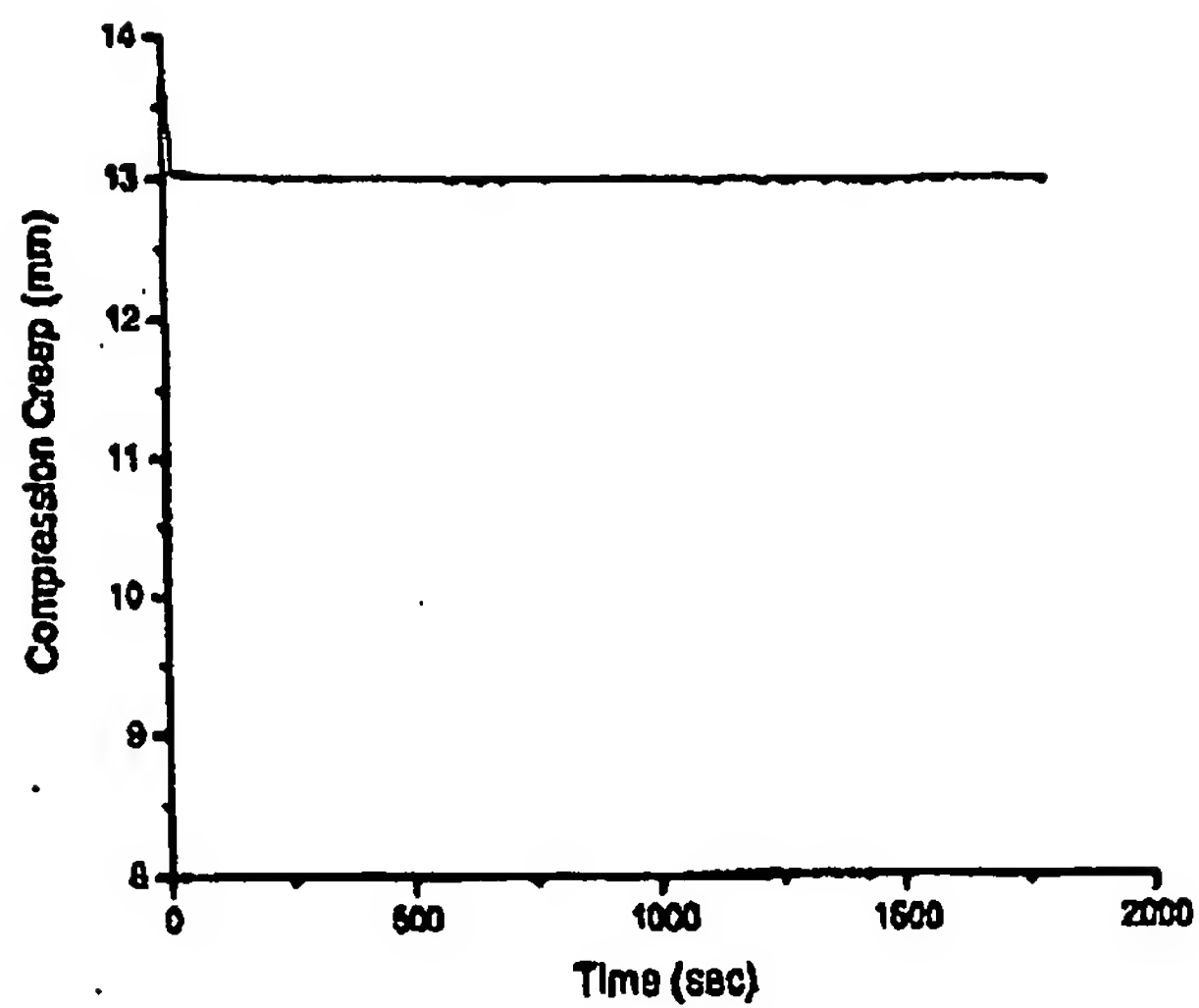


FIGURE 6

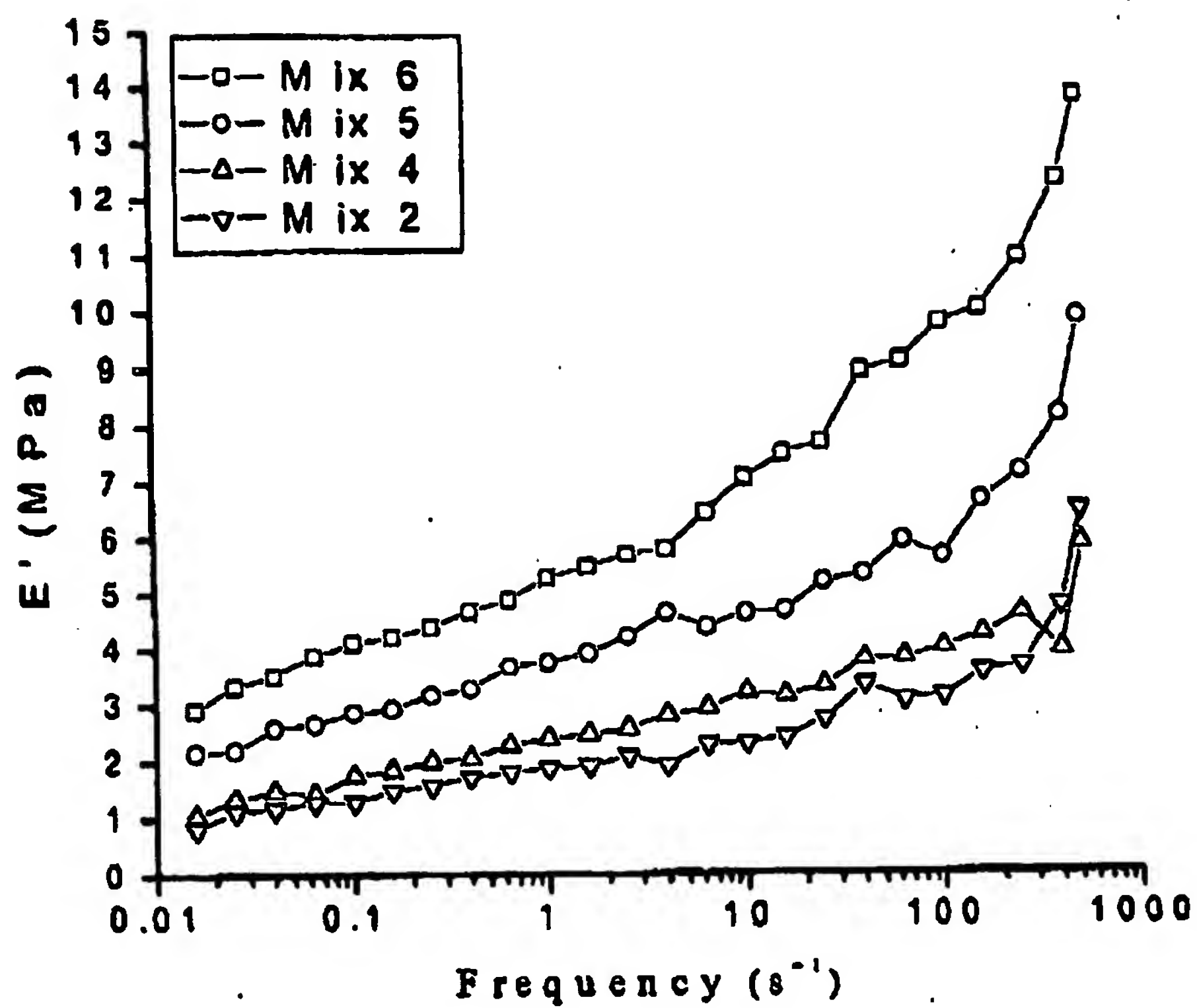


FIGURE 7

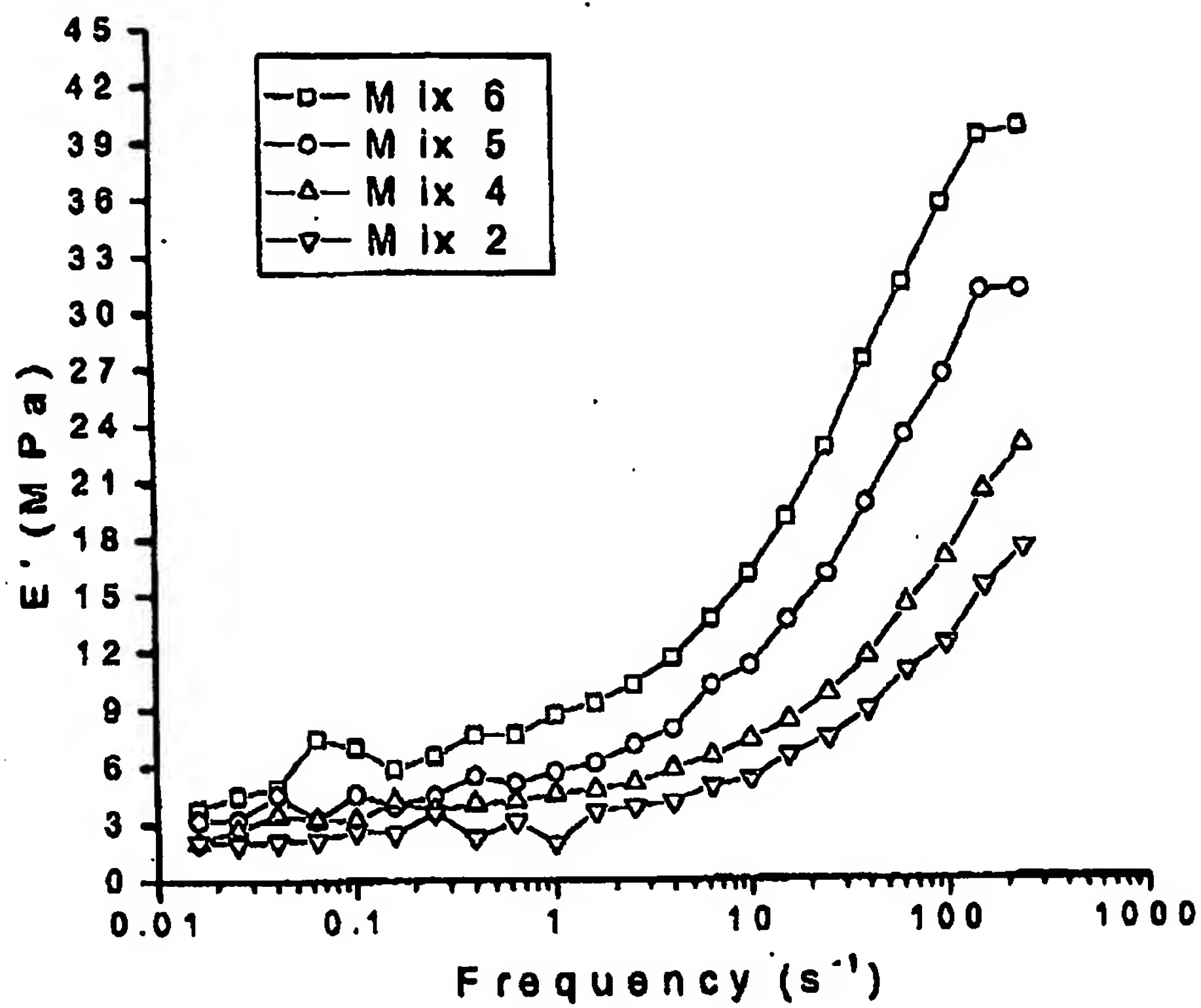


FIGURE 8

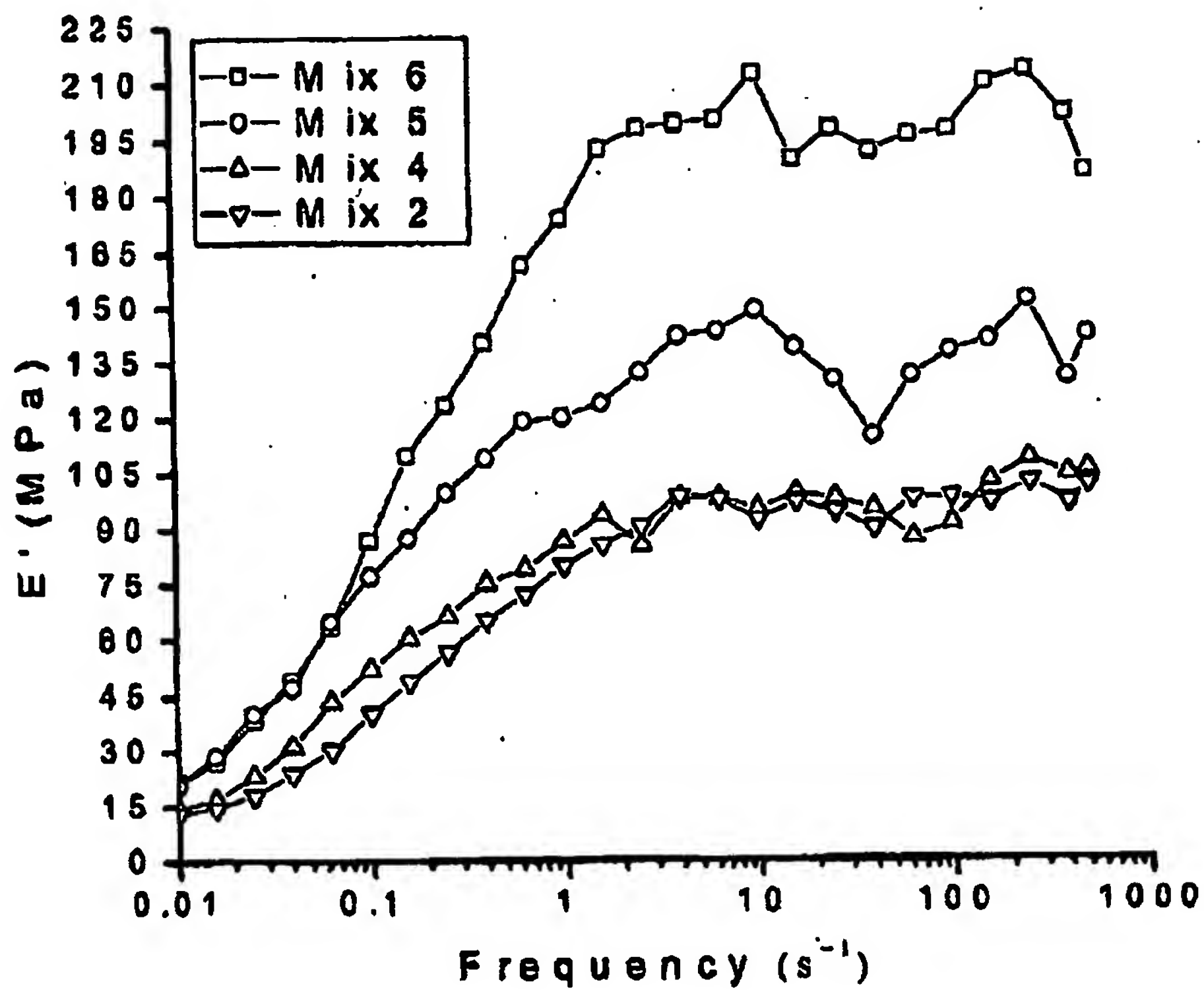


FIGURE 9

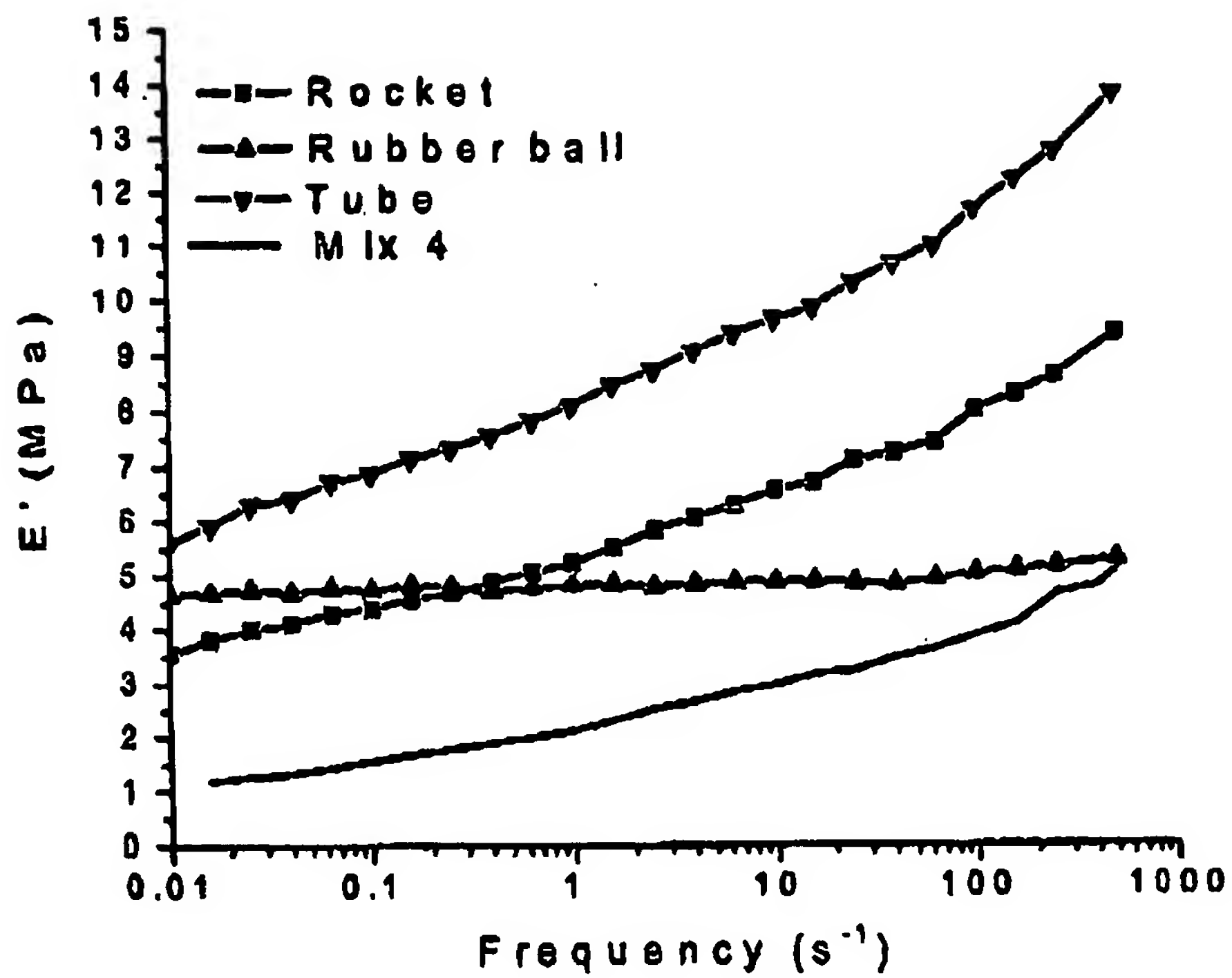


FIGURE 10

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